

EVALUATION OF IMPACT RESULTING FROM HOME HEATING OIL TANK DISCHARGES

Summary and Findings of Look-Back Study

Mark A. Widdowson, P.I.
Gabriel Isaacman-VanWertz, co-P.I.

The Charles E. Via, Jr. Department of Civil & Environmental Engineering
Virginia Tech

August 28, 2018
Revised October 18, 2018
Updated October 26, 2018

1. Purpose and Scope

The purpose of this technical memorandum is to summarize an investigation of potential impacts of petroleum discharges from home heating oil tanks on domestic drinking water wells and surface water bodies. This report describes methods for determining sampling locations, methods for sampling and analysis, and results of contaminant concentrations.

To summarize the results, HHO-derived volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) were not detected in any water well samples or surface water samples at levels at or above the individual compound-specific Maximum Contaminant Levels (MCLs). No HHO-derived compounds were detected in any water samples collected at control sites.

This work is a component to a study of potential impacts at residences in the Virginia Department of Environmental Quality (DEQ) home heating oil (HHO) tank program. Water samples were collected primarily from domestic wells of homeowners in the DEQ HHO tank program. Water samples were also collected at homes in which a surface water body was within 300 ft of the former underground storage tank (UST). Domestic wells of homes not in the DEQ HHO tank program were identified and sampled and served as control wells. Drinking water samples were also collected at several number of homes in the DEQ HHO tank program that receive potable water from a public water supply as an additional control sample. Analysis for the concentration of HHO-derived VOCs and SVOCs in water samples was conducted in the Environmental Engineering Laboratory on the Virginia Tech campus in Blacksburg.

2. Approach and Methods

2.1. Site Selection and Sampling Plan

Site Characterization Reports were ultimately the source of information on drinking water supplied to homes in the DEQ HHO tank program. The reports indicate the source of drinking water for the residence impacted by an UST discharge. Reports also identify potable water well receptors and surface waters within a 1,000 feet radius of the site. This information was not available in an accessible database.

Similar to the petroleum vapor intrusion (PVI) study in which a stratified random sampling plan was designed to determine the PVI test sites, the look-back study employed the same methodology with some key differences. The PVI random sample consisted of two factors: (1) geographic location using the three major physiographic regions in Virginia (Valley and Ridge, Piedmont, and Coastal Plain); and (2) DEQ category. All residential cases were considered for the PVI study. The random sampling for the look-back study only considered residential cases with domestic wells and focused on a subset of the total population of residential cases (described below). Wells with known petroleum impacts and already investigated by DEQ were not included within this study. Within the subset identified as potential well owners, random sampling of cases was weighted by physiographic region and DEQ Category.

As a precursor to the random sampling of the subset, GIS tools were utilized to eliminate cases at locations in cities, towns, and other metropolitan areas where a public water supply was likely available. As a result, the random sampling primarily targeted cases located in rural areas of Virginia. Using three strata, one per physiographic region, and three substrata, one per DEQ category, cases were assigned to the appropriate stratum. Cases were selected randomly in numbers proportionate to the physiographic region and DEQ category. For surface water sampling, GIS tools were again utilized to identify cases from the entire population of residential case in which former USTs were located within 300 ft of surface water bodies.

A list of 401 randomly selected cases were provided to DEQ with a request to provide Site Characterization Reports. These reports were then reviewed to confirm whether an active domestic well was located on the property within 300 ft of the former UST and utilized for potable drinking water. Homeowners whose case number was selected randomly and with a confirmed well used for potable water were contacted by letter explaining the nature and scope

of the look-back study. The letter provided contact information in the event of interest in participating. The response rate was less than 10%. Homeowners who responded were contacted, and sampling events were scheduled. Cases with surface water in proximity were sampled in conjunction with trips to conduct water sampling or in conjunction with trips associated with the PVI investigation.

For the purpose of this study, control sites were defined by one of two categories determined by the source of potable water: (1) domestic wells and (2) public water supply. Any domestic wells located at residences not in the DEQ HHO tank program served as control wells. Specifically, no reported release of heating oil occurred at any of the control sites or no other known source of petroleum hydrocarbon compounds had impacted the domestic wells used as controls. These controls served as controls to verify the hypothesis that petroleum hydrocarbons compounds were not present in domestic wells at residences where no release of heating oil has previously occurred. The second category of controls were residences in the DEQ HHO tank program that were not supplied with potable water from a domestic well but received water through a public water supply system. Samples in this category served as negative controls to support the hypothesis that petroleum hydrocarbons compounds were absent from water supplied to homes not supplied by a domestic well but where a heating oil release was documented.

2.2. Methodologies

2.2.1. Sample Collection

Resources utilized for development of plans for water sample collection and field preservation included the DEQ Storage Tank Program Quality Assurance Project Plan—State Lead Program (Rev. No. 2, 2013), Standard Operating Procedures Manual for the DEQ Water Monitoring and Assessment Program (Rev. No. 19, 2014), EPA Quick Guide to Drinking Water Sample Collection (2nd ed., 2015), and EPA Region 4 Science and Ecosystem Support Division Surface Water Sampling Operating Procedure (2013).

Drinking water samples were preferably collected from a faucet inside the residence. In the event that was not possible, samples were collected from an outside spigot. Location identified based on accessibility, and bypassing of a water filtration system or aerator. Cold water was run between 5 to 15 minutes prior to sampling to flush the system and acquire a more representative sample of the well water. Sampling containers were labeled based on household

numerical address. For each household, water samples using two 500-mL amber glass bottles were collected first for the analysis of 17 polycyclic aromatic hydrocarbon (PAH) compounds. In addition, two 40-mL amber glass bottles with Teflon caps were filled for analysis of benzene, toluene, ethyl-benzene, m,p-xylene, and o-xylene (BTEX) and MTBE (methyl tertiary-butyl ether). Finally, 250-mL Nalgene bottle for possible analysis of metals and inorganics as a contingency if petroleum-derived hydrocarbon compounds were detected. For every sampling trip, three 500-mL and 40-mL amber glass bottles were collected for QA/QC as determined by the EPA analysis method.

The 500-mL and the 250-mL bottles were filled with the sampled water entirely. The 40-mL bottles were overfilled to form a meniscus, the cap secured tightly, and the bottles inverted to make sure there were no air bubbles present. If air bubbles were detected, the bottles were topped off to re-establish the meniscus. Bottles for each household were kept in separate 2-gallon plastic bags and stored in cooler with ice during sampling trip. All samples were store in the 4-degree room located in the Virginia Tech Environmental Engineering Laboratory. All samples were processed and analyzed within the 7-day holding time as mandated by the EPA method.

2.2.2. Laboratory Methods

The BTEX and MTBE analysis was performed by purge and trap using the 6890 GC-FID EPA method 502 on a Restek Rxi-624Sil MS GC column. A calibration curve was run prior to running the samples, using standards prepared from the stock solution of BTEX and MTBE mix. A 5-mL gas tight syringe was used to remove 5-mL of sample from the sample container and loaded onto the autosampler valve. For every batch a 5ppb BTEX/MTBE standard and check were run at the beginning and end of each batch. A temperature program, calibration curve standards, and a detailed standard operating procedure were developed for analysis of BTEX and MTBE including an appropriate level of standard checks, blanks, and duplicate runs. Quality Assurance/Quality Control (QA/QC) procedures for BTEX and MTBE analysis are provided in the Appendix.

Samples were prepared for PAH analysis using Solid Phase Extraction EPA Method 3500C. For the 500-mL bottles, 25 microliters of the 100 mg/l working stock of the surrogate standards was added directly into the sample bottle before extraction for an extracted concentration of 5 mg/L. The entire 500-mL samples were extracted onto SPE cartridges through

a manifold using a vacuum pump. After complete filtration of samples, the PAH compounds were eluted from the cartridges into GC autosampler vials using methylene chloride. The solvent was evaporated for a final volume of 0.5 mL. For every 20 samples, a matrix spike and a matrix spike duplicate samples were run per QA/QC measures. Samples were analyzed for PAH compounds using Thermo Scientific-Focus GC with DSQ II mass spec with column Restek Rxi-5 Sil MS (length 30m, ID 0.25mm, Film thickness 0.5 um) following the EPA method 8270 (SW-846). The 17 PAH compounds analyzed were: naphthalene, 2-methylnaphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenz(a,h)anthracene, and benzo(g,h,i)perylene. QA/QC procedures for PAH analysis are provided in the Appendix.

3. Results

MTBE and BTEX concentrations in water samples are presented in **Table 1**. The results are organized by group. The groups and number of samples collected and analyzed are: Domestic wells in the DEQ HHO program (24 cases); Surface water within 300-ft of former USTs (5 cases); Controls (6). Duplicate samples at three wells were collected and analyzed for MTBE and BTEX. PAH concentrations in water samples are presented in **Table 2**.

Overall, the results show no detection of TEX compounds or MTBE in any samples. Benzene was detected in one sample collected from a domestic well but at a concentration (0.29 µg/L) well below the MCL. The results show no detection of any of the PAH compounds in any samples. Given these results, no relationship between the proximity of the well to the former USTs or Physiographic Region (**Table 3**) could be developed.

4. Summary of Findings

Although impacts to groundwater, including domestic wells, due to UST discharges has been documented at residential cases in the DEQ HHO program, there were no indications of any impacts to the domestic wells sampled due to petroleum hydrocarbons. BTEX, MTBE, and PAH compounds were not detected in any of the surface water samples.

5. References

- APHA, AWWA, and WEF (American Public Health Association, American Water Works Association, and Water Environment Federation). 1998. Standard Methods for Examination of Water and Wastewater, 20th ed. Washington, D.C.: APHA.
- Virginia Department of Environmental Quality. 2013. Storage Tank Program Quality Assurance Project Plan—State Lead Program, Rev. No. 2, 11/19/13, 60 p.
- Virginia Department of Environmental Quality. 2014. Standard Operating Procedures Manual for the DEQ Water Monitoring and Assessment Program, Rev. No. 19, 2/27/14, 158 p.
- Virginia Department of Environmental Quality. 2014. Storage Tank Program Quality Assurance Project Plan—Alternative Water Supply Program, Rev. No. 2, 8/4/14, 75 p.
- USEPA Region 4. 2013. Science and Ecosystem Support Division Surface Water Sampling Operating Procedure, SESDPROC-201-R3, 22 p.
- USEPA Region 8. 2015. Quick Guide to Drinking Water Sample Collection, 2nd ed., November 2015, 20 p.

Table 1. MTBE and BTEX Concentrations (µg/L) in Water Samples.

ID	MTBE	Benzene	Ethylbenzene	Toluene	m,p Xylene	o Xylene
Cases with Domestic Wells in Home Heating Oil Tank Program						
20082022	BD	BD	BD	BD	BD	BD
20092013	BD	BD	BD	BD	BD	BD
20097077	BD	BD	BD	BD	BD	BD
20112251	BD	BD	BD	BD	BD	BD
20116073	BD	BD	BD	BD	BD	BD
20122133	BD	BD	BD	BD	BD	BD
20122281	BD	BD	BD	BD	BD	BD
20124483	BD	BD	BD	BD	BD	BD
20132080	BD	BD	BD	BD	BD	BD
20132080D	BD	BD	BD	BD	BD	BD
20132098	BD	BD	BD	BD	BD	BD
20134245	BD	BD	BD	BD	BD	BD
20142021	BD	BD	BD	BD	BD	BD
20142021D	BD	BD	BD	BD	BD	BD
20142205	BD	0.29	BD	BD	BD	BD
20152089	BD	BD	BD	BD	BD	BD
20152185	BD	BD	BD	BD	BD	BD
20152198	BD	BD	BD	BD	BD	BD
20152435	BD	BD	BD	BD	BD	BD
20156135	BD	BD	BD	BD	BD	BD
20162136	BD	BD	BD	BD	BD	BD
20162136D	BD	BD	BD	BD	BD	BD

ID	MTBE	Benzene	Ethylbenzene	Toluene	m,p Xylene	o Xylene
20162224	BD	BD	BD	BD	BD	BD
20162299	BD	BD	BD	BD	BD	BD
20162374	BD	BD	BD	BD	BD	BD
20172038	BD	BD	BD	BD	BD	BD
20172041	BD	BD	BD	BD	BD	BD
Surface Water						
20124030	BD	BD	BD	BD	BD	BD
20124391	BD	BD	BD	BD	BD	BD
20132123	BD	BD	BD	BD	BD	BD
20145107	BD	BD	BD	BD	BD	BD
20146061	BD	BD	BD	BD	BD	BD
Controls						
C6188-22318	BD	BD	BD	BD	BD	BD
C216-22618	BD	BD	BD	BD	BD	BD
20124137	BD	BD	BD	BD	BD	BD
20122231	BD	BD	BD	BD	BD	BD
20145107	BD	BD	BD	BD	BD	BD
NCW1	BD	BD	BD	BD	BD	BD

Table 2. PAH Concentrations (µg/L) in Water Samples.

Sample ID	Naphthalene	2-Methylnaphthalene	Acenaphthylene	Acenaphthene	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Benz(a)anthracene	Chrysene	Benz(b)fluoranthene	Benz(k)fluoranthene	Benzo(a)pyrene	Indeno(1,2,3-cd)pyrene	Dibenz(a,h)anthracene	Benzo(g,h,i)perylene
Cases with Domestic Wells in Home Heating Oil Tank Program																	
20082022	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD
20092013	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD
20097077	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD
20112251	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD
20116073	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD
20122133	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD
20122281	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD
20124483	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD
20132080	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD
20132098	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD
20134245	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD
20142021	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD

Sample ID	Naphthalene	2-Methylnaphthalene	Acenaphthylene	Acenaphthene	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Benz(a)anthracene	Chrysene	Benzo(b)fluoranthene	Benzo(k)fluoranthene	Benzo(a)pyrene	Indeno(1,2,3-cd)pyrene	Dibenz(a,h)anthracene	Benzo(g,h,i)perylene
20142205	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD
20152089	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD
20152185	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD
20152198	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD
20152435	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD
20156135	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD
20162136	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD
20162136D	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD
20162224	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD
20162299	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD
20162374	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD
20172038	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD
20172041	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD

Sample ID	Naphthalene	2-Methylnaphthalene	Acenaphthylene	Acenaphthene	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Benz(a)anthracene	Chrysene	Benzo(b)fluoranthene	Benzo(k)fluoranthene	Benzo(a)pyrene	Indeno(1,2,3-cd)pyrene	Dibenz(a,h)anthracene	Benzo(g,h,i)perylene
Surface Water																	
20124137	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD
20124398	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD
20132123	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD
20145107	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD
20146061	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD
Controls																	
C6188-22318	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD
C216-22618	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD
20124137	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD
20122231	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD
20145107	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD
NCW1	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD

Table 3. Case ID and Site Characteristics.

Cases with Domestic Wells in Home Heating Oil Tank Program		
	Physiographic Region	Distance (well to UST area, ft)
20082022	Piedmont	119
20092013	Valley & Ridge	80
20097077	Piedmont	79
20112251	Piedmont	35
20116073	Piedmont	43
20122133	Piedmont	65
20122281	Blue Ridge	75
20124483	Piedmont	50
20132080	Piedmont	23
20132098	Piedmont	120
20134245	Piedmont	80
20142021	Piedmont	30
20142205	Piedmont	5
20152089	Piedmont	190
20152185	Piedmont	Not reported
20152198	Piedmont	153
20152435	Piedmont	60
20156135	Blue Ridge	30
20162136	Blue Ridge	75
20162224	Piedmont	50
20162299	Piedmont	47
20162374	Piedmont	30
20172038	Valley & Ridge	100
20172041	Piedmont	70

Cases with nearby Surface Water (SW)		
	Physiographic Region	Distance (well to SW, ft)
20124030	Piedmont	52
20124391	Coastal Plain	290
20132123	Valley & Ridge	80
20145107	Coastal Plain	60
20146061	Piedmont	100

Appendix – QA/QC for Laboratory Procedures

Quality Control for BTEX and MTBE analysis by Purge and Trap

- 1) Sample Collection Requirements and holding times
 - a. 40 ml vials with septa closure
 - b. Store at <6 C in dark. If chlorine present: Preserve-0.008% Na₂SO₄
 - c. Holding time: 14 days
- 2) Minimum Reporting Level for PAHs: 0.5 ug/l (Lowest standard on calibration curve)
- 3) QC-Samples required
 - a. Method Blanks: Before processing any samples, the analyst should demonstrate that all parts of the equipment contacting the sample and reagents are interference-free. This is accomplished through the analysis of a method blank. Each time samples are extracted, cleaned up, and analyzed, a method blank should be prepared and analyzed for the compounds of interest as a safeguard against chronic laboratory contamination. Method blanks should be prepared at a frequency of at least one method blank for each group of up to 20 samples prepared at the same time, by the same procedures. The method blank should be analyzed immediately after the calibration verification standard to ensure that there is no carryover from the standard or at another point in the analytical shift. ***The laboratory should not subtract the results of the method blank from those of any associated samples. Such "blank subtraction" is inappropriate for the GC.***
 - b. Laboratory Control Spike (LCS): The LCS is spiked with method analytes and is processed identically to the samples (extracted same as samples). One LCS should be done per sample preparation batch. **Acceptable criteria for recoveries of spiked analytes is 70 - 130% recovery.**
 - c. Matrix Spikes (MS)/Matrix Spike Duplicates (MSD): At least one matrix spike and one matrix spike duplicate should be prepared and analyzed with each batch of up to 20 samples of the same matrix processed together. When the lab does not receive enough samples to perform a single matrix spike, an LCS and LCS duplicate (LCSD) may be performed to document precision and bias. **Acceptable criteria for recoveries of spiked analytes is 70 - 130%. Relative % difference should be <20%.** If % recovery and RPD are outside these ranges data maybe in question.
 - d. Calibration verification standard (CVS): Prepared in the same matter as initial calibration standards. At a minimum should be analyzed at the beginning of each batch of samples ran in a given day. **Acceptable criteria for recoveries of analytes is 80 - 120%.** If the recovery for an analyte meets this criteria, then the initial calibration for that compound is assumed to be valid. Due to the large numbers of compounds that may be analyzed, it is expected that some compounds will fail to meet the criterion. If more than 20% of the compounds included in the initial calibration do not pass, then corrective action must be taken prior to the analysis of samples. In cases where compounds fail, they may still be reported as non-detects if it can be demonstrated that there was adequate sensitivity to detect the compound at the applicable quantitation limit. For situations when the failed compound is present, the concentrations must be reported as estimated values.

- 4) To demonstrate Method Proficiency: Prepare and analyze at least four replicate aliquots of a reference standard using the same procedures that were used to analyze actual samples. Calculate the mean recovery and the standard deviation of the recovery (s) for each analyte of interest using the four results.

5) Calculations:

a. Surrogate Recoveries

$$\text{Recovery (\%)} = \frac{\text{Concentration found}}{\text{Concentration added}} \times 100$$

b. MS/MSD, Duplicate, and LCS Recoveries

$$\text{MS/MSD and LCS Recovery (\%)} = \frac{(C_s - C_u)}{C_n} \times 100$$

Where

C_s = Measured concentration of spiked sample

C_u = Measured concentration of unspiked sample (use 0 for LCS)

C_n = Concentration increase added to sample (for LCS ultra pure water)

Relative Percent Difference (RPD) for MS/MSD

$$\text{RPD} = \frac{\frac{|C_1 - C_2|}{(C_1 + C_2)}}{2} \times 100$$

Calculations continued:

c. Sample Concentration (ug/l) for aqueous samples extracted and concentrated

$$\text{Concentration in ug/l} = \frac{(X_s) (V_t) (D)}{(V_s)}$$

Where

X_s = Calculated concentration of analyte (ng/ul) from calibration curve

V_t = Volume of concentrated extract in ul.

D = Dilution factor (if needed)

V_s = Initial volume of sample extracted in ml

References:

1. EPA SW-846: Method 8000D, "DETERMINATIVE CHROMATOGRAPHIC SEPARATIONS"
2. EPA SW-846: Method 8021-Flame Ionization Detector was used in place of Photoionization Detector
3. VA DEQ: "Quality Assurance Project Plan (QAPP)- Storage Tank Program"

Quality Control for PAH analysis by GCMS

- 1) Sample Collection Requirements and holding times
 - a. 1-liter brown glass bottle with PTFE lined cap
 - b. Store at <6 C in dark. If chlorine present add Na₂S₂O₃
 - c. Holding time: 7 days prior to extraction/40 days after extraction
- 1) Minimum Reporting Level for PAHs: 2 ug/l (from VA DEQ QAPP)
- 2) Calibration by Internal Standards: A constant amount of the internal standard (i.e., a compound that is chemically similar to the analyte group but is not expected to occur in an environmental sample) is added to all extracts (post extraction). That same amount of the internal standard is also included in each of the calibration standards. In the sample or sample extract, the peak response ratio of the target compound to the internal standard is compared with a similar ratio derived for each calibration standard. This ratio is termed the response factor (RF) or relative response factor (RRF), indicating that the target compound response is calculated relative to that of the internal standard. The GCMS software will calculate these responses. Advantages of internal standard calibration include that it can account for routine change in response of the chromatographic system as well as variation in the volume of the introduced sample extract. A minimum of five different concentrations within the working range of the instrument are needed. The lowest standard concentration analyzed must at the minimum reporting level.
- 3) Surrogate (i.e., a compound that is chemically similar to the analyte group but is not expected to occur in an environmental sample) should be added to each sample, blank, laboratory control sample (LCS), and matrix spike sample just prior to extraction or processing. The recovery of the surrogate standard is used to monitor for unusual matrix effects, gross sample processing errors, etc. **Acceptable criteria for recoveries of surrogate analytes is 70 - 130%.**
- 4) QC-Samples required
 - e. Method Blanks: Before processing any samples, the analyst should demonstrate that all parts of the equipment contacting the sample and reagents are interference-free. This is accomplished through the analysis of a method blank. Each time samples are extracted, cleaned up, and analyzed, a method blank should be prepared and analyzed for the compounds of interest as a safeguard against chronic laboratory contamination. Method blanks should be prepared at a frequency of at least one method blank for each group of up to 20 samples prepared at the same time, by the same procedures. The method blank should be analyzed immediately after the calibration verification standard to ensure that there is no carryover from the standard or at another point in the analytical shift. ***The laboratory should not subtract the results of the method blank from those of any associated samples. Such "blank subtraction" is inappropriate for the GC.***
 - f. Laboratory Control Spike (LCS): The LCS is spiked with method analytes and is processed identically to the samples (extracted same as samples). One LCS should be done per sample preparation batch. **Acceptable criteria for recoveries of spiked analytes is 70 - 130% recovery.**

- g. Matrix Spikes (MS)/Matrix Spike Duplicates (MSD): At least one matrix spike and one matrix spike duplicate should be prepared and analyzed with each batch of up to 20 samples of the same matrix processed together. When the lab does not receive enough samples to perform a single matrix spike, an LCS and LCS duplicate (LCSD) may be performed to document precision and bias. **Acceptable criteria for recoveries of spiked analytes is 70 - 130%. Relative % difference should be <20%.** If % recovery and RPD are outside these ranges data may be in question.
- h. Calibration verification standard (CVS): Prepared in the same matter as initial calibration standards. At a minimum should be analyzed at the beginning of each batch of samples ran in a given day. **Acceptable criteria for recoveries of analytes is 80 - 120%.** If the recovery for an analyte meets this criteria, then the initial calibration for that compound is assumed to be valid. Due to the large numbers of compounds that may be analyzed, it is expected that some compounds will fail to meet the criterion. If more than 20% of the compounds included in the initial calibration do not pass, then corrective action must be taken prior to the analysis of samples. In cases where compounds fail, they may still be reported as non-detects if it can be demonstrated that there was adequate sensitivity to detect the compound at the applicable quantitation limit. For situations when the failed compound is present, the concentrations must be reported as estimated values.
- 5) To demonstrate Method Proficiency: Prepare and analyze at least four replicate aliquots of a reference standard using the same procedures that were used to analyze actual samples. Calculate the mean recovery and the standard deviation of the recovery (s) for each analyte of interest using the four results.
- 6) Calculations:

d. Surrogate Recoveries

$$\text{Recovery (\%)} = \frac{\text{Concentration found}}{\text{Concentration added}} \times 100$$

e. MS/MSD, Duplicate, and LCS Recoveries

$$\text{MS/MSD and LCS Recovery (\%)} = \frac{(C_s - C_u)}{C_n} \times 100$$

Where

C_s = Measured concentration of spiked sample

C_u = Measured concentration of unspiked sample (use 0 for LCS)

C_n = Concentration increase added to sample (for LCS ultra pure water)

Relative Percent Difference (RPD) for MS/MSD

$$\text{RPD} = \frac{\frac{|C_1 - C_2|}{(C_1 + C_2)}}{2} \times 100$$

Calculations continued:

f. Sample Concentration (ug/l) for aqueous samples extracted and concentrated

$$\text{Concentration in ug/l} = \frac{(X_s) (V_t) (D)}{(V_s)}$$

Where

X_s = Calculated concentration of analyte (ng/ul) from calibration curve

V_t = Volume of concentrated extract in ul.

D = Dilution factor (if needed)

V_s = Initial volume of sample extracted in ml

References:

- 1) EPA SW-846: Method 8000D, "DETERMINATIVE CHROMATOGRAPHIC SEPARATIONS"
- 2) EPA SW-846: Method 8270D, "SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY"
- 3) EPA SW-846: Method 3500C, "ORGANIC EXTRACTION AND SAMPLE PREPARATION"
- 4) VA DEQ: "Quality Assurance Project Plan (QAPP)- Storage Tank Program"